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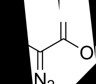

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[redacted]Amino acid; α-Diazo carbonyl compounds; Imine; Regio-
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[redacted]ponding author. Tel.: +86 10 6275 7248; fax: +86 10 6275 7248;
[redacted]ail: wangjb@pku.edu.cn

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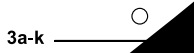
Table 1. -(tosyl) imine **2a–m**

Entry		Product	Yield (%)[a]
1		**3a**	54
2		**3b**	81
3		**3c**	57
4		**3d**	90
5		**3e**	60
6		**3f**	76
7		**3g**	51
8		**3h**	67
9		**3i**	83
10		**3j**	47
11	$_3$	**3k**	57
12		**3l**	72
13		**3m**	82

[a] Th silica gel column chromatography.

ge ith *m*-chloroperbenzoic acid (*m* dimethyldioxirane (DMD).[8] We fo o compounds **3a–k**, the oxidation oc h commercially available Oxone® (p osulfate) directly. Since, the prep- a oxirane from Oxone® requires low t e yield is usually low,[9] the direct eap Oxone® greatly simplifies the tion and also makes use of the oxidant he oxidation of **3l** and **3m** under the sa mplex mixture (Scheme 2).

β-(*N*-tosyl)amino esters **6a–k**



then proceeded to study t ester **6a** was taken as a r with $NaBH_4$ at 0 °C in TH tosyl)amino ester **4a** excl (300 MHz) of the crude pr was 82%. On the other h hydrogenated with Pd/C (room temperature, the *syn* **5a** was formed, with hi isolated yield. The assignm the comparison of the spe reported known compound

The scope and limitations reduction with $NaBH_4$ and catalyst were summarized the reduction with Na generally high diaste on the other hand cases.[12] For α-c to give the e substitue

The

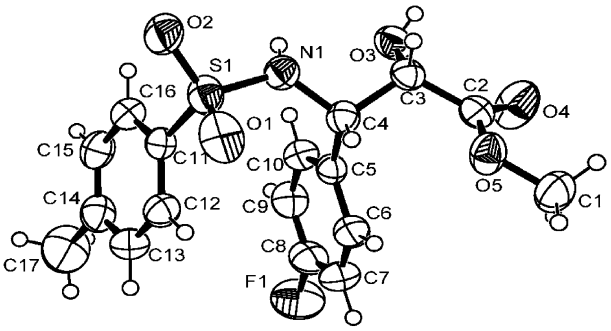


Figure 1. -ray structure of **4c**.

a chair form conformation due to the hydrogen bonding. In the reduction with $NaBH_4$, the hydride is delivered from the axial direction to give the product with *anti* configuration, in which hydroxyl group occupies the equatorial position.[14]

Another way to interpret the stereochemical process is by the Newman projection **7** shown in Figure 2. The hydride reagent attacks the carbonyl group from the sterically less hindered direction to provide the *anti* product. This is similar to the metal chelation controlled reduction of α-ketols.[15] On the other hand, the Felkin's model **8**, in which it is assumed there is no intramolecular hydrogen bonding between the *N*-tosylamino group and the carbonyl group, predicts the *syn* product to be predominant.[16]

To confirm the role of the hydrogen bonding, we studied the corresponding reduction and hydrogenation with compound **9**, in which the hydrogen on the amino group was replaced with a methyl group. The reduction with $NaBH_4$ gave the α-hydroxyl products with essentially no diastereoselectivity (Scheme 5). Thus, the experimental result supported the proposed role of hydrogen bonding.

For the hydrogenation catalyzed with Pd/C, it was conceivable that the chair conformation exposed the less sterically hindered bottom face to hydrogen delivery and thus, providing the *syn* product (Scheme 6).[17] When compound **9** was subjected to the hydrogenation condition, it was found that the reaction became complicated. ^{1}H NMR spectrum of the crude product indicated the formation of *syn* product **11** in low yield. However, there was no *anti* product **10** identified from the ^{1}H NMR spectrum.

In summary, a novel approach to both *anti*- and *syn*-α-hydroxy β-amino acid derivatives with high diastereoselectivities has been developed. This approach requires only three steps from the easily available aryl (*N*-tosyl)-imine and methyl diazoester.[18] If the enantioselectivity can be controlled in the first step of the nucleophilic condensation, this approach can be further developed into a method to prepare non-racemic *syn*- and *anti*-α-hydroxy β-amino acid derivatives.[19] The investigation along this direction is currently under the way in our laboratory.

3. Experimental

3.1. General methods

^{1}H and ^{13}C NMR spectra were recorded at 300 MHz (or 200 MHz) and 75 MHz (or 50 MHz) with Varian Mercury 300 (or 200) spectrometer, or at 400 and 100.6 MHz with Brucker AR 400 spectrometer. The chemical shifts were reported in ppm using TMS as the internal standard. All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask, and the components were added

via syringe. All solvents were distilled prior to use according to standard procedures. THF was distilled over sodium. For chromatography, 100–200 mesh silica gel (Qindao, China) was employed. IR spectra were recorded with a Nicolet 5M -S infrared spectrometer. HPLC analysis was performed at HP 1100 apparatus with Chiracel column. Mass spectra were obtained on a VG ZAB-HS mass spectrometer.

3.2. General procedure for the reaction of methyl diazoacetate with aryl (*N*-tosyl)imines

(a) *With DBU as the base*. To a solution of methyl diazoacetate (1.0 mmol) in anhydrous MeCN (8 mL) was added DBU (0.25 mmol) at room temperature under N_2. Then the imine (0.85 mmol) was added. The reaction mixture was stirred at room temperature for about 1 h. The solvent was removed and the crude product was purified by column chromatography with petroleum ether/EtOAc.

(b) *With NaH as the base*. To a solution of methyl diazoacetate (1.0 mmol) in anhydrous THF (8 mL) was added 60% NaH (43 mg, 1.25 equiv), then the imine (0.85 mmol) was added, the reaction mixture was stirred for 1 h and quenched with saturated aqueous $NaHCO_3$ at 0 °C. The resulting slurry was extracted with CH_2Cl_2 (3× 15 mL). Usual work up gave a crude product, which was purified by column chromatography.

3.2.1. Methyl 2-diazo-3-phenyl-3-[(*N*-tosyl)amino] propanoate (3a). IR (film) 3262, 2097, 1691 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.43 (s, 3H), 3.62 (s, 3H), 5.33 (d, J= 7.6 Hz, 1H), 5.60 (w, 1H), 7.28–7.30 (m, 7H), 7.35 (d, J= 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.2, 51.7, 53.2, 126.0, 126.8, 128.0, 128.5, 129.2, 136.7, 137.3, 143.3, 165.4; EI-MS (*m/z*, relative intensity) 331 [$(M-28)^+$, 16], 260 (17), 164 (20), 139 (40), 91 (100). Anal. Calcd for $C_{17}H_{17}O_4N_3S$: C, 56.81; H, 4.77; N, 11.69. Found: C, 56.84; H, 4.79; N, 11.68.

3.2.2. Methyl 2-diazo-3-(*p*-phenyl)phenyl-3-[(*N*-tosyl)-amino]propanoate (3b). IR (film) 3265, 2098, 1697 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.40(s, 3H), 3.61(s, 3H), 5.40 (d, J=7.5 Hz, 1H), 5.89 (d, J=7.5 Hz, 1H), 7.26–7.55 (m, 11H), 7.75 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 51.9, 53.5, 126.7, 126.9, 127.1, 127.4, 128.7, 129.5, 136.4, 136.8, 140.1, 141.1, 143.6, 165.6; EI-MS (*m/z*, relative intensity) 407 [$(M-28)^+$, 54], 375 (6), 220 (33), 193 (42), 164 (76), 91 (100); HRMS calcd for $C_{23}H_{21}NSO_4$ $(M-28)^+$ 407.1191, found 407.1200.

3.2.3. Methyl 2-diazo-3-(*p*-fluoro)phenyl-3-[(*N*-tosyl)-amino]propanoate (3c). IR (KBr) 3442, 2113, 1687 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 3.61(s, 3H), 5.32 (d, J=4.5 Hz, 1H), 5.72 (s, 1H), 6.95–7.01 (m, 2H), 7.23–7.31 (m, 4H), 7.72 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 51.9, 53.4, 115.6, 115.9, 127.1, 128.1, 128.2, 129.6, 133.4, 136.8, 143.9, 165.5; EI-MS (*m/z*, relative intensity) 349 [$(M-28)^+$, 27], 164 (29), 155 (32), 91 (100); HRMS calcd for $C_{17}H_{16}NSO_4F$ $(M-28)^+$ 349.0784, found 349.0794.

3.2.4. Methyl 2-diazo-3-(*p*-chloro)phenyl-3-[(*N*-tosyl)-amino]propanoate (3d). IR (KBr) 3548, 2111, 1686 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 3.59 (s, 3H), 5.31(d, J=7.4 Hz, 1H), 5.73(d, J=7.4 Hz, 1H), 7.19–7.36 (m, 6H), 7.71 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.5, 52.0, 53.6, 127.1, 127.8, 129.0, 129.7, 134.4, 136.1, 136.8, 143.9, 165.5; EI-MS (*m/z*, relative intensity) 365 [$(M-28)^+$, 100], 333 (14), 304 (6), 178 (12), 91 (5); HRMS calcd for $C_{17}H_{16}NSO_4^{35}Cl$ $(M-28)^+$ 365.0489, found 365.0497.

3.2.5. Methyl 2-diazo-3-(*o*-methyl)phenyl-3-[(*N*-tosyl)-amino]propanoate (3e). IR (film) 3266, 2097, 1697 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.23 (s, 3H), 2.43 (s, 3H), 3.62 (s, 3H), 5.27 (d, J=5.0 Hz, 1H), 5.50 (d, J=5.0 Hz, 1H), 7.15–7.30 (m, 6H), 7.75 (d, J=8.4 Hz, 2H); ^{13}C NMR (75 MHz) δ 18.9, 21.4, 50.1, 125.9, 126.3, 127.2, 128.2, 129.4, 130.8, 135.1, 136.6, 143.5, 165.6; EI-MS (*m/z*, relative intensity) 345 [$(M-28)^+$, 10], 274 (9), 258 (8), 158 (28), 130 (58), 91 (100); HRMS calcd for $C_{18}H_{19}NO_4S$ 345.1035, found 345.1037.

3.2.6. Methyl 2-diazo-3-(*p*-methoxy)phenyl-3-[(*N*-tosyl)-amino]propanoate (3f). IR (KBr) 3446, 2103, 1684 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.43 (s, 3H), 3.62 (s, 3H), 3.77 (s, 3H), 5.28 (d, J=7.2 Hz, 1H), 5.52 (d, J=7.2 Hz, 1H), 6.79–6.85 (m, 2H), 7.15–7.21 (m, 2H), 7.29 (d, J= 8.6 Hz, 2H), 7.73(d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.5, 51.9, 53.5, 55.3, 114.2, 127.2, 127.6, 129.6, 129.6, 136.8, 143.7, 159.6, 165.7; EI-MS (*m/z*, relative intensity) 361 [$(M-28)^+$, 26], 329 (6), 290 (19), 164 (44), 147 (48), 132 (52), 91 (100). Anal. Calcd for $C_{18}H_{19}O_5N_3S$: C, 55.52; H, 4.92; N, 10.79. Found: C, 55.62; H, 4.99; N, 10.75.

3.2.7. Methyl 2-diazo-3-(*m*-trifluoromethyl)phenyl-3-[(*N*-tosyl)amino]propanoate (3g). IR (KBr) 3452, 2104, 1645 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.36 (s, 3H), 3.57 (s, 3H), 5.37 (d, J=7.8 Hz, 1H), 5.99 (d, J=7.8 Hz, 1H), 7.20–7.66 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 52.0, 53.7, 123.2, 125.1, 127.0, 127.3, 129.4, 129.7, 129.8, 130.9, 136.7, 138.7, 144.0, 165.4; EI-MS (*m/z*, relative intensity) 399 [$(M-28)^+$, 6], 164 (22), 155 (24), 139 (32), 91 (100); HRMS calcd for $C_{18}H_{16}NO_4SF_3$ 399.0752, found 321.0761.

3.2.8. Methyl 2-diazo-3-(*m*-bromo)phenyl-3-[(*N*-tosyl)-amino]propanoate (3h). IR (KBr) 3213, 2106, 1673 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3H), 3.61 (s, 3H), 5.33 (d, J=8.0 Hz, 1H), 5.94 (d, J=8.0 Hz, 1H), 7.13–7.69 (m, 6H), 7.71 (d, J=1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 52.0, 53.4, 122.8, 124.9, 127.0, 129.4, 130.3, 131.4, 136.7, 139.8, 143.9, 165.4; EI-MS (*m/z*, relative intensity) 409 [$(M-28)^+$, 5], 279 (18), 167 (28), 149 (100); HRMS calcd for $C_{17}H_{16}NSO_4^{79}Br$: 408.9983, found 408.9983.

3.2.9. Methyl 2-diazo-3-(*m*-cyano)phenyl-3-[(*N*-tosyl)-amino]propanoate (3i). IR (KBr) 3427, 2103, 1749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.45 (s, 3H), 3.62 (s, 3H), 5.23 (d, J=8.8 Hz, 1H), 6.07 (d, J=8.8 Hz, 1H), 7.27–7.82 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 52.1, 53.4, 112.7, 118.2, 126.2, 126.9, 129.6, 129.7, 131.0, 131.8, 136.6, 139.2, 144.1, 165.3; EI-MS (*m/z*, relative intensity) 356 [$(M-28)^+$, 18], 292 (4), 164 (16), 155 (25), 91 (100), 65 (20); HRMS calcd for $C_{18}H_{16}N_2SO_4$ 356.0831, found 356.0827.

3.2.10. Methyl 2-diazo-3-(2,4-dichloro)phenyl-3-[(*N*-tosyl)amino]propanoate (3j). IR (KBr) 3189, 2110, 1659 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, 3H), 3.59 (s, 3H), 5.58 (d, $J=8.2$ Hz, 1H), 6.21 (d, $J=8.2$ Hz, 1H), 7.13–7.40 (m, 5H), 7.71 (d, $J=8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 51.2, 51.9, 127.0, 127.2, 129.4, 129.5, 129.6, 132.8, 133.8, 134.5, 136.6, 143.9, 165.4; EI-MS (*m*/*z*, relative intensity) 399 [$(M-28)^+$, 8], 364 (10), 332 (9), 164 (16), 155 (30), 91 (10); HRMS calcd for $C_{17}H_{15}NO_4SCl_2$ 399.0099, found

J=9.6 Hz, 1H), 6.92 (d, J=8.4 Hz, 2H), 7.05–7.26 (m, 4H), 7.47 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 52.9, 58.5, 73.3, 126.9, 128.4, 128.9, 129.4, 133.4, 134.2, 137.4, 143.4, 171.3; EI-MS (*m/z*, relative intensity) 294 [$(M-89)^+$, 63], 155 (83), 91 (100); HRMS calcd for $C_{14}H_{13}NSO_2Cl$: 294.0356, found 294.0362.

3.3.5. *trans*-Methyl 2-hydroxy-3-(*o*-methyl)phenyl-3′-(*N*-tosylamino)propanoate (4e). IR (KBr) 3445, 2361, 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, 3H), 2.32 (s, 3H), 3.17 (br, 1H), 4.54 (dd, J=4.2, 6.6 Hz, 1H), 5.94 (dd, J=4.2, 9.3 Hz, 1H), 5.74 (br, 1H), 6.91–7.16 (m, 6H), 7.50 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.0, 21.4, 52.5, 54.2, 72.9, 126.1, 126.8, 127.1, 127.9, 129.2, 130.4, 133.7, 135.3, 137.4, 143.1, 171.8; EI-MS (*m/z*, relative intensity) 274 [$(M-89)^+$, 100], 155 (54), 91 (100); MS (MALDI-TOF): 402 $(M+K)^+$, 386 $(M+Na)^+$; HRMS calcd for $C_{15}H_{16}NSO_2$ 274.0902, found 274.0902.

3.3.6. *trans*-Methyl 2-hydroxy-3-(*p*-methoxyl)phenyl-3′-(*N*-tosylamino)propanoate (4f). IR (film) 3286, 1741, 1252 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 2.94 (d, J=6.8 Hz, 1H), 3.66 (s, 3H), 3.73 (s, 3H), 4.50 (dd, J=3.4, 6.8 Hz, 1H), 4.78 (dd, J=3.4, 9.5 Hz, 1H), 5.65 (d, J=9.5 Hz, 1H), 6.63 (d, J=7.9 Hz, 2H), 6.91 (d, J=7.9 Hz, 2H), 7.08 (d, J=8.1 Hz, 2H), 7.52 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 52.7, 55.2, 58.6, 73.6, 113.6, 126.9, 127.0, 128.5, 129.3, 137.6, 143.0, 159.4, 171.6; EI-MS (*m/z*, relative intensity) 290 [$(M-89)^+$, 100], 134 (23), 91 (84); HRMS calcd for $C_{15}H_{16}O_3NS$: 290.0851, found 290.0845.

3.3.7. *trans*-Methyl 2-hydroxy-3-(*m*-bromo)phenyl-3′-(*N*-tosylamino)propanoate (4h). IR (film) 3283, 1741, 1333, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 3.35 (d, J=5.9 Hz, 1H), 3.67 (s, 3H), 4.57 (dd, J=3.3, 5.9 Hz, 1H), 4.81 (dd, J=3.3, 9.6 Hz, 1H), 6.15 (d, J=9.6 Hz, 1H), 6.98–7.52 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.4, 52.8, 58.7, 73.4, 122.2, 126.2, 126.7, 126.8, 129.3, 129.7, 130.7, 130.9, 136.9, 137.0, 143.3, 171.3; EI-MS (*m/z*, relative intensity) 340 [$(M-89)^+$, 63], 338 (60), 155 (100), 91 (99), 77 (20), 51 (11); HRMS calcd for $C_{14}H_{13}O_2NSBr$: 337.9850, found 337.9848.

3.3.8. *trans*-Methyl 2-hydroxy-3-(*m*-cyano)phenyl-3′-(*N*-tosylamino)propanoate (4i). IR (film) 3271, 1742, 1333, 1159 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 2.98 (d, J=5.2 Hz, 1H), 3.69 (s, 3H), 4.55 (dd, J=3.4, 5.2 Hz, 1H), 4.87 (dd, J=3.4, 9.3 Hz, 1H), 5.68 (d, J=9.3 Hz, 1H), 7.10–7.50 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 53.0, 58.4, 73.1, 112.3, 118.0, 126.8, 129.0, 129.5, 131.3, 131.6, 132.1, 136.4, 137.1, 143.7, 171.1; EI-MS (*m/z*, relative intensity) 286 [$(M-89)^+$, 14], 285 (78), 156 (10), 155 (93), 91 (100), 65 (22); HRMS calcd for $C_{15}H_{13}O_2N_2S$: 285.0698, found 285.0693.

3.3.9. *trans*-Methyl 2-hydroxy-3-(2,4-dichloro)phenyl-3′-(*N*-tosylamino)propanoate (4j). IR (KBr) 3447, 2361, 1631 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3H), 3.08 (d, J=6.6 Hz, 1H), 3.68 (s, 3H), 4.59 (dd, J=3.9, 6.6 Hz, 1H), 5.33 (d, J=3.9, 9.7 Hz, 1H), 5.80 (d, J=9.7 Hz, 1H), 6.97–7.57 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 29.7, 52.8, 54.6, 72.5, 126.9, 127.1, 129.4, 130.4, 131.5, 133.6, 134.6, 136.8, 143.6, 171.5; EI-MS (*m/z*, relative intensity) 328 [$(M-89)^+$, 52], 155 (74), 91 (100); MS (MALDI-TOF): 456 $(M+K)^+$, 440 $(M+Na)^+$, 418 $(M+H)^+$; HRMS for $C_{14}H_{12}NSO_2^{35}Cl_2$ 327.9966, found 327.9968.

3.3.10. *trans*-Methyl 2-hydroxy-3-(2,6-dichloro)phenyl-3′-(*N*-tosylamino)propanoate (4k). IR (KBr) 3450, 2362, 1745 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3H), 2.86 (d, J=9.3 Hz, 1H), 3.86 (s, 3H), 4.62 (t, J=9.3 Hz, 1H), 5.44 (dd, J=9.3, 11.1 Hz, 1H), 6.03 (d, J=11.1 Hz, 1H), 6.99–7.28 (m, 6H), 7.56–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 29.7, 52.9, 56.8, 71.5, 126.7, 128.6, 129.2, 129.5, 129.7, 131.5, 133.3, 136.8, 143.3, 172.5; EI-MS (*m/z*, relative intensity) 328 [$(M-89)^+$, 46], 155 (58), 91 (100); MS (MALDI-TOF): 456 $(M+K)^+$, 440 $(M+Na)^+$; HRMS for $C_{14}H_{12}NSO_2^{35}Cl_2$ calcd 327.9966, found 327.9973.

3.4. General procedure for the hydrogenation of α-oxo compounds 6a–f catalyzed with Pd/C

To a solution of α-oxo compound **6a–f** (0.1 mmol) in anhydrous MeOH (15 mL) was added 10% Pd/C catalyst (10 mg). The reaction mixture was stirred for 24 h under 1 atm hydrogen atmosphere. Then Pd/C catalyst was removed by fast column chromatography with MeOH as the eluent. The solvent was evaporated to give a crude residue, which was purified by column chromatography with petroleum ether, $CHCl_3$, and MeOH to give the pure product of **5a–f**. The melting points of white solid **5a–f** were not obtained due to the isomerization of *syn* and *anti* at high temperature.

3.4.1. *cis*-Methyl 2-hydroxy-3-phenyl-3′-(*N*-tosylamino)-propanoate (5a). IR (film) 3281, 1738, 1158 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 3.31 (d, J=4.5 Hz, 1H), 3.76 (s, 3H), 4.35 (dd, J=4.5, 2.4 Hz, 1H), 4.85 (dd, J=9.2, 2.4 Hz, 1H), 5.75 (d, J=9.2 Hz, 2H), 7.07–7.26 (m, 7H), 7.53 (d, J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 53.2, 58.9, 74.2, 126.9, 127.0, 127.8, 128.4, 129.3, 137.4, 137.5, 143.2, 172.5. EI-MS (*m/z*, relative intensity) 260 [$(M-89)^+$, 100], 155 (41), 91 (54). MS (MALDI-TOF) 388 $(M+K)^+$, 372 $(M+Na)^+$. Anal. Calcd for $C_{17}H_{19}O_5NS$: C, 58.44; H, 5.48; N, 4.01. Found: C, 58.39; H, 5.63; N, 3.76.

3.4.2. *cis*-Methyl 2-hydroxy-3-(*p*-phenyl)phenyl-3′-(*N*-tosylamino)propanoate (5b). IR (KBr) 3303, 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.28 (s, 3H), 3.34 (d, J=4.2 Hz, 1H), 3.78 (s, 3H), 4.39 (br, 1H), 4.91(d, J=9.8 Hz, 1H), 5.75 (d, J=9.8 Hz, 1H), 7.06–7.55 (m, 13H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 53.3, 58.8, 74.2, 126.9, 127.1, 127.4, 128.8, 129.3, 136.3, 136.4, 137.5, 137.6, 140.5, 140.8, 143.2, 172.5; EI-MS (*m/z*, relative intensity) 336 [$(M-89)^+$, 100], 180 (18), 155 (36), 91 (83). MS (MALDI-TOF): 448 $(M+K)^+$, 464 $(M+Na)^+$. Anal. Calcd for $C_{23}H_{23}O_5NS$: C, 64.92; H, 5.45; N, 3.29. Found: C, 65.08; H, 5.30; N, 3.14.

3.4.3. *cis*-Methyl 2-hydroxy-3-(*p*-fluoro)phenyl-3′-(*N*-tosylamino)propanoate (5c). IR(KBr) 3445, 2361, 1713 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H),

3.45 (br, 1H), 3.77 (s, 3H), 4.32 (s, 1H), 4.83 (dd, J=2.1, 9.9 Hz, 1H), 5.93 (d, J=9.9 Hz, 1H), 6.79–7.14 (m, 6H), 7.52 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.3, 53.2, 58.4, 74.2, 115.0, 115.3, 126.9, 128.7, 128.8, 129.3, 133.2, 137.4, 143.3, 160.6, 163.9, 172.4; EI-MS (*m/z*, relative intensity) 278 [$(M-89)^+$, 68], 155 (66), 91 (100); HRMS calcd for $C_{14}H_{13}NSO_2F$: 278.0651, found 278.0648.

3.4.4. *cis*-Methyl 2-hydroxy-3-(*p*-chloro)phenyl-3′-(*N*-tosylamino)propanoate (5d). IR (KBr) 3448, 2361, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 3.16 (d, J=4.0 Hz, 1H), 3.76 (s, 3H), 4.35 (dd, J=4.0, 2.3 Hz, 1H), 4.85 (dd, J=2.3, 9.8 Hz, 1H), 5.47 (d, J=9.8 Hz, 1H), 7.09–7.20 (m, 6H), 7.52 (d, J=8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 53.3, 58.9, 74.1, 126.8, 127.0, 127.9, 128.4, 129.3, 137.4, 137.5, 143.2, 172.4. EI-MS (*m/z*, relative intensity) 327 [$(M-56)^+$, 5], 294 [$(M-89)^+$, 14], 260 (100), 155 (76), 91 (100); HRMS calcd for $C_{14}H_{13}NSO_2Cl$: 294.0356, found 294.0357.

3.4.5. *cis*-Methyl 2-hydroxy-3-(*o*-methyl)phenyl-3′-(*N*-tosylamino)propanoate (5e). IR (KBr) 3269, 2361, 1749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3H), 3.44 (br, 1H), 3.79 (s, 3H), 4.24 (br, 1H), 5.15 (dd, J=2.1, 9.7 Hz, 1H), 6.02 (d, J=9.7 Hz, 1H), 6.95–7.10 (m, 6H), 7.48 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.1, 21.3, 53.2, 54.9, 73.1, 126.0, 126.8, 127.4, 129.1, 130.2, 134.3, 135.3, 137.3, 142.9, 172.7; EI-MS (*m/z*, relative intensity) 274 [$(M-89)^+$, 74], 155 (58), 91 (100); HRMS calcd for $C_{15}H_{16}NSO_2$: 274.0902 [$(M-89)^+$], found 274.0904.

3.4.6. *cis*-Methyl 2-hydroxy-3-(*p*-methoxyl)phenyl-3′-(*N*-tosylamino)propanoate (5f). IR (film) 3282, 1739, 1250, 1158 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.33 (s, 3H), 3.32 (d, J=4.6 Hz, 1H), 3.74 (s, 6H), 4.31 (dd, J=2.4, 4.6 Hz, 1H), 4.78 (dd, J=2.4, 9.6 Hz, 1H), 5.71 (d, J=9.6 Hz, 1H), 6.66–6.71 (m, 2H), 7.03–7.26 (m, 4H), 7.53 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.4, 53.1, 55.2, 58.6, 74.3, 113.7, 127.0, 128.0, 129.2, 129.4, 137.5, 143.0, 159.1, 172.6; EI-MS (*m/z*, relative intensity) 290 [$(M-89)^+$, 100], 155 (38), 134 (21), 92 (10); HRMS calcd for $C_{15}H_{16}O_3NS$: 290.0851, found 290.0844.

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